

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Ethylene Copolymer Shrinkable Films

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to films from copolymers of ethylene with other ethylenically unsaturated compounds. More particularly it relates to improved shrinkable films of copolymers of ethylene with ethylenically unsaturated carboxylic acids, ethylenically unsaturated carboxylic esters, and ethylenically unsaturated nitriles; and to the preparation of such films.

A particularly desirable property of a shrinkable film is higher shrinkability below about 100°C., i.e., below the boiling point of water. In many of the uses of shrinkable film, as in the packaging of heat-sensitive foods, a greater degree of shrinkage at such lower temperatures is desirable to avoid the risk of partial cooking or discoloration. Another desideratum is higher shrink tension to provide neater appearing, tighter packages, especially in the case of irregularly shaped articles, and concurrently therewith additional film strength so that the film will not break during such greater shrinkage. For the packaging of produce and fresh meats, greater permeability for oxygen and carbon dioxide is advantageous.

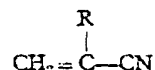
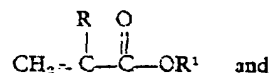
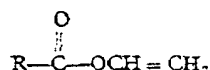
This invention provides a shrinkable film which has a greater percentage shrink at temperatures below about 100°C. than has heretofore been available. It further provides a shrink film which requires a low radiation dose in its preparation, which has a high shrink energy, or shrink tension, and greater dimensional shrink than is present in previously available films, a greater permeability to oxygen and carbon dioxide, less relaxation

with time at usual ambient temperatures, and greater strength and resistance to impact.

It has now been found that improved shrinkable films are obtained by a process comprising the steps:

(1) making a thin, coherent film of a copolymer of ethylene with from 1 to 45, preferably from 3 to 20, percent by weight of at least one monovinylidene monomer such as the vinyl esters of C₂ to C₄ alkanolic monocarboxylic acids, C₁ to C₄ alkyl esters of α,β-ethylenically unsaturated monocarboxylic acids, α,β-ethylenically unsaturated monocarboxylic acids, or α,β-ethylenically unsaturated nitriles, (2) irradiating the resulting polymer film with a dose of ionizing radiation of from 1 to 20 megarads, (3) placing the irradiated film under stress to produce orientation in at least one direction while the film is maintained at a temperature of from 85° to 200°C., and (4) cooling the film to below 70°C. while maintaining said stress.

The monovinylidene monomers (referred to in this specification as the minor component of the polymer, for brevity) which are copolymerized with ethylene to produce the polymers used in the practice of this invention may be represented by the formulae:



wherein R and R¹ are hydrogen or alkyl radicals having from 1 to 4 carbon atoms.

One or a mixture of two or more of the

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monovinylidene monomers can be used as the minor component in making the ethylene copolymers for use in this invention.

5 If desired, in the copolymers useful in the present invention there may be substituted for a portion of the ethylene small proportions, i.e. up to about 2 percent, of other α -ethyl-
10 enically unsaturated hydrocarbons. (Such substituted monomers are not included within the term "minor component" as described elsewhere in this specification.)

When about one percent of the copolymer weight consists of the interpolymers of minor component, such as acrylic acid, the copolymer
15 when used in the practice of this invention produces a film having improved shrink properties compared to the shrinkable films of the prior art. In general the percent shrink and the shrink tension of the treated film is
20 increased as the percentage of the minor component in the copolymer is increased up to about 20 percent by weight. For example copolymers of ethylene and acrylic acid where-
25 in the acrylic acid component proportions were 3, 8, and 15 percent by weight when subjected to the procedure of this invention showed an area shrinkage of about 67, 87 and 91 per-
30 cent, respectively. Shrink tension also increases in a similar manner with an increase in minor component proportion.

While from 3 to 20 percent by weight of the minor component is preferred to give the desired community of properties, certain properties, e.g. the transmission of moisture and
35 of gases such as carbon dioxide and oxygen, are improved when even a higher proportion, i.e. up to 45 percent by weight, of the minor component, is used. Although the copolymers which may be used advantageously in the
40 preparation of shrinkable films contain from 1 to 45 percent by weight of the minor component, the optimum proportion required to obtain the best films, and the proportion required to obtain equivalent films will be
45 different for the different minor components. Thus, for example, the same area shrink, i.e. about 86 percent at 100°C., was obtained from ethylene copolymers containing respec-
50 tively by weight 20 percent ethyl acrylate, 11 percent vinyl acetate and 7.5 percent acrylic acid in interpolymers of form when the films were given the same dose of high energy
55 ionizing radiation, i.e. 8 megarads of high speed electrons.

The molecular weight of the copolymers useful in the present invention are usually from 18,000 to 46,000 or more as calculated from a measurement of their intrinsic viscosities.

60 Optionally, other polymers and copolymers, e.g., linear polyethylene, polypropylene, ethylene-propylene copolymers, and vinyl chloride-vinylidene chloride copolymers, can be blended with the ethylene copolymers here-
65 tofore described for use in the practice of this invention.

Small amounts of conventional additives and modifiers useful in the resin plastics art, such as antioxidants, stabilizers, antistatic agents, antiblocking agents, slip agents, pigments, colorants, and the like, can be com-
70 pounded with the copolymers which are used in preparing the shrink films of this invention. Likewise, ultraviolet sensitizers may be adsorbed on the copolymer or blended there-
75 with if ultraviolet radiation is to be used in the irradiation step of the process.

In the practice of this invention a thin coherent film of the ethylene copolymers here-
80 tofore described is prepared by conventional techniques such as solution casting, solution extrusion, heat (melt) extrusion through an annular or a flat die, calendaring and the like. Such a film advantageously has a thickness
85 of from about 5 mils to about 60 mils (0.127 to 1.5 mm.), preferably from 12 mils to 40 mils (0.3 to 1.0 mm.). In a typical procedure the polymer is extruded at a temperature
90 preferably from 140° to 200°C. through an annular die of a conventional extruder to form a tube. Air at low pressure, such as about 2 pounds per square inch (14 kg/sq.cm.) may
95 be introduced through the center of the die mandrel to assist in controlling the size of the tube, if desired. In a non-continuous process, the tubing may then be cooled and
100 rolled onto spools. The tubing is later unwound from the spool and brought to irradiation temperature. Alternatively, in a continuous process, the tubing, after extrusion from the
105 die may be cooled only sufficiently that it does not flow, or to a predetermined lower temperature, and then fed directly to the irradiation zone. The irradiation step is advantageously carried out at a temperature from
110 room temperature to about 90°C. The irradiation may be accomplished by use of any of various sources. High energy electrons emitted by a resonant transformer or a Van de Graaff
115 generator are preferred for the irradiation step but various radioactive elements such as cobalt-60, iron-59, strontium-90, phosphorus-32 and carbon-14 and the like which produce β - or gamma-rays upon decay; and X-rays or ultraviolet rays having wave lengths between
120 about 2000 and about 2700 Angstroms may be used if desired.

The radiation dose rate is not critical provided the required total dose is obtained. Ordinarily, however, the rate of accumulation
125 of the radiation is greater than about 0.04 megarads per hour. The preferred dose of radiation is from two to ten megarads. Generally less than one megarad of radiation will not produce the desired results and more than
130 ten megarads up to about 20 megarads, while producing a shrinkable film, is not as desirable because then the irradiated tubing becomes more difficult to stretch, the area of film obtainable per kg. of polymer is decreased, and the increased cost of the irradiation

tion makes production of the film uneconomical. Also the strength, percent area shrink and shrink tension become impaired at high doses of radiation.

- 5 The tube is irradiated by passing it through the irradiation zone in such a manner as to provide a substantially uniform dose throughout. Increased radiation efficiency can be obtained by multiple passes of the tubing in the path of the radiation beam. The optimum number of passes will depend on the tubing thickness, the rate of movement of the tubing through the beam and the radiation intensity of the beam.

- 15 After the irradiation step, the tubing is heated to a temperature preferably from 100° to 120°C. and is oriented at that temperature such as by blowing the tube to a size of about 2 to about 10 times its original diameter by means of a gas, e.g. air or nitrogen, inserted into the tubing under low pressure.

- 25 The direction or dimension along the length of the tubing is considered the machine, (or longitudinal, or length) dimension of any film produced from it and the direction perpendicular thereto is known as the transverse, or width, dimension.

- 30 Concurrently with the blowing operation the film may be stretched longitudinally by rollers which pull it from the heated zone at a rate which is faster than that at which the tubing was introduced. The ratio of the output roll speed to the input speed often is from about 1.4 to about 5.00. Other methods of producing the orientation also may be used such as by stretching in a plane in a length and/or transverse direction a flat section of the irradiated film placed inside a heated chamber.

- 40 The stretched film is maintained under the same degree of stress while it is cooled below 70°C. Optionally, the irradiated, oriented film may then be rolled onto spools.

- 45 In many applications for shrinkable film, especially where it is desired to print on packaging material, the shrink must be

approximately equal in the length and the width directions. For such applications the orientation produced by the stretching operation should be substantially the same in the transverse as in the longitudinal direction. However, there are instances where a greater degree of shrink may be desired in one direction than another, e.g. in packaging objects in which an air-tight seal is not essential, the ends of a tubular sleeve may be shrunk around the ends of an object in a width direction (due to the predominance of transverse orientation) without appreciable shrinking in the longitudinal direction. The amount of stretching during the orientation step in length, width or area must be at least as great as the amount of shrink desired in that dimension in the oriented, irradiated film.

The amount of orientation built into the tube during its extrusion, and the draw-down ratio; i.e. the ratio of the input speed of the tube to the output speed of the blown film, are factors which affect the shrinkage of the final film product. Any orientation put into the tube during the extrusion process reduces the orientation which can be introduced by the blowing and stretching process; after irradiation, thus lessening the shrinkability of the film.

The following descriptions illustrate typical methods for testing the properties of films useful as shrinkable packaging materials and these methods were used in testing the films of the present invention.

Percent Shrink

A single-thickness film sample, 4" x 4". (10 x 10 cm.) is cut and the machine direction is marked. The sample is then placed in a heated and circulated silicone oil bath held at a predetermined temperature $\pm 0.5^\circ\text{C}$. The sample is allowed to remain in the bath for at least one minute before being removed, cooled and the machine (longitudinal) and transverse dimensions measured.

Calculations are made according to the formulae:

$$\text{Percent Length Shrink} = \frac{(\text{original dimension} - \text{final dimension}) \text{ longitudinal}}{\text{original dimension (longitudinal)}} \times 100$$

$$\text{Percent Width Shrink} = \frac{(\text{original dimension} - \text{final dimension}) \text{ transverse}}{\text{original dimension (transverse)}} \times 100$$

$$\text{Percent Area Shrink} = \frac{\text{Original area} - \text{Final area}}{\text{Original Area}} \times 100$$

Shrink Tension

Shrink tension, sometimes referred to as shrink energy, is defined as the force exerted by a film as it shrinks at a given temperature, divided by the cross-sectional area of the sample, the result being expressed in grams or pounds per unit area. For the shrink tension measurement, a single-thickness sample 1" x 3" (2.5 x 7.6 cm.), is cut and then placed between two supporting members — one member being connected to the force measuring arm and the other member being static. While the sample is in place a hot bath, such as of water, ethylene glycol, air, etc., is so placed as to immerse the sample therein and thus shrink it. The bath may be held in place until the force reaches its peak, or it can be held in place for a predetermined time with the measurements being registered to determine the value at different time intervals.

Creep

The property called "creep" is the elongation, or relaxation, with time under a particular stress. The creep extension usually is expressed as a percentage of the initial unstressed length. One method of determining creep is to prepare a sample as in the Shrink Tension Test and to clamp one end of the sample to a stationary support and hang a pre-determined weight from the other end of the sample. A measurement of the length of the sample is made immediately after shrinking and cooling, then additional measurements are made at different time intervals thereafter. The amount of elongation, or relaxation, is determined by subtracting the original measurement from each of the subsequent measurements. The percent elongation at a particular time interval is calculated by the formula:

$$\frac{\text{amount of elongation}}{\text{original length}} \times 100.$$

Data may be recorded for samples tested in the machine or in the transverse directions. As discussed in ASTM D674-56, results from creep testing usually are plotted in various forms of graphs to facilitate interpolation and extrapolation, as well as interpretation.

Melt Index

The melt index was determined by the method of ASTM D1238-57T.

The following examples are set forth to illustrate more clearly the principles and practice of this invention to those skilled in the art and are not for the purpose of limitation. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A copolymer of ethylene consisting of 13

percent by weight of interpolymerized vinyl acetate and having a melt index of 2.0 was extruded with pressure at a temperature of 160°C. through an annular die to form a tube having a diameter of 2.7 cm and a wall thickness of 15 mils (0.38 mm.). The tube was cooled in air and then wound onto a spool. Because of its flexibility, the tube became somewhat flattened during the winding operation. The flattened tube, without preheating was irradiated twice, once on each side, by effecting two passes of the tube under the beam of an electron generator at a rate of two inches (5 cm.) per second which caused a substantially uniform penetration of the tubing. The generator was operated at a beam current of 5.0 milliamperes and 1.04 million electron volts. Thus, the tubing received a total dose of about 8 megarads. The irradiated tube was heated to a temperature of between 100° and 120°C. and an internal air pressure of two pounds per square inch (0.14 kg./sq.cm.) was supplied to blow the tube to a diameter of 14 cm. The blown tube was also stretched by means of tension produced by rollers at a draw-down ratio of 4.2 to give the film orientation in a longitudinal direction. The resulting biaxially oriented irradiated film was cooled to room temperature while the air pressure and the tension of the rollers were maintained.

EXAMPLE 2

A copolymer of ethylene containing 13.6 percent by weight of interpolymerized vinyl acetate and having a melt index of 2.0 was processed as shown in Example 1 except for the following changes: the tube diameter was 2.65 cm, the tube was preheated to 90°C. immediately prior to the irradiation step, and the rate of movement through the electron beam was 1.67 inches, (4.2 cm.) per second to give a total radiation dose of about 12 megarads. The area shrink at 100°C. of the final film product was 89 percent and the shrink tension was 410 pounds per square inch (48.7 kg./sq.cm.).

EXAMPLE 3

A copolymer of ethylene containing 20 percent by weight of interpolymerized ethyl acrylate and having a melt index of 2.0 was treated as in Example 1 except that the extruded tube had a diameter of 2.96 cm and a wall thickness of 16 mils, (0.4 mm.) the irradiation dose was about 12 megarads at a temperature of 41°C., and the tube was blown to a diameter of 12.36 cm and to a wall thickness of 2.1 mils (0.053 mm.). The film product had a shrink tension of 340 lb./sq. in. (23.8 kg./sq.cm.) at 100°C. The percent area shrink was 67.2 at 85°C., and 86.5 at 100°C.

EXAMPLE 4

A series of ethylene copolymers containing different percentages by weight of interpolymerized acrylic acid were treated according to the procedure of Example 1 using a radiation dose of 8 megarads. Table I shows the percentage shrink in width, length and area.

TABLE I

Ethylene Copolymer Film		Percentage of Shrink at the Indicated Temperature								
Melt Index	Percent Acrylic Acid in Copolymer	96° C.			98° C.			101° C.		
		W	L	A	W	L	A	W	L	A
2.0	2.9	25	20	40	31	26	48	50	35	67
2.0	8.0	38	35	60	45	42	68	72	55	87
2.0	15.0	50	45	72	55	52	79	73	66	91

W = width
L = length
A = area

The copolymer containing 15 percent of interpolymerized acrylic acid had a shrink tension of 236 lb./sq.in. (16.5 kg/sq.cm.) at 97°C. and 316 lb./sq.in. (22 kg/sq.cm.) at 99°C.

EXAMPLE 5

A copolymer of ethylene containing 7.5 percent by weight of acrylonitrile and having a melt index of 10 was extruded at a temperature of 200°C. to form a tube 2.25 cm. in diameter and having a wall thickness of 25 mils (0.635 mm.). The tube of polymer was given an 8-megarad dose of ionizing radiation under the beam of a General Electric Resonant Transformer operated at a potential of one-million electron volts and a beam current of 5 milliamperes at a temperature of 25°C. The irradiated tube was heated to 110°C. and

blown and stretched to form a biaxially oriented film having a thickness of 1.6 mils (0.04 mm.). After the film was cooled under tension, the shrink was found to be the same in the length and the width direction, being 47 percent at 96°C., 56 percent at 98°C. and 65 percent at 101°C.; the area shrink at those temperatures was 72, 81 and 88 percent, respectively.

EXAMPLE 6

Other shrink films were prepared from the copolymers and by the procedures of Examples 2 and 3 except that the total radiation dosage and the irradiation temperature were varied. The shrink tensions of the resulting films were measured in the transverse direction at 100°C. The results are shown in Table II.

TABLE II

Shrink Tension

(Kg./sq. cm. at 100° C.)

Ethylene Copolymer Film			Temperature of Irradiation °C.			
Minor Component	Percent	Dose Megarad	25	40	70	90
Vinyl Acetate	13.6	4	3.7	4.48	9.45	4.0
Vinyl Acetate	13.6	8	22.5	22.3	24.8	22.5
Vinyl Acetate	13.6	12	29.8	31.2	35.0	28.6
Ethyl Acrylate	20	4	0	3.4	8.68	2.45
Ethyl Acrylate	20	8	8.46	8.96	11.75	10.8
Ethyl Acrylate	20	12	9.25	24.0	Not measured	16.4

EXAMPLE 7

The irradiated oriented films of Example 6 which were irradiated at 25°C. with a total

dose of 8 megarads were tested for the percent shrink in area at 70°, 80°, and 90°C. The results are shown in Table III.

TABLE III

Ethylene Copolymer Film		Percent Shrink in Area at Shrink Temperature of:		
Minor Component	Percent	70° C.	80° C.	90° C.
Vinyl Acetate	13.6	15	26	53
Ethyl Acrylate	20.0	22	42	78

EXAMPLE 8

A copolymer of ethylene containing 10 percent by weight of ethyl acrylate and having a melt index of 2.0 was extruded at 200°C. to form a tube 2.25 cm. in diameter and having a wall thickness of 25 mils (.635 mm.). The tubing was irradiated under the beam of an electron generator operated at a potential

of one million electron volts at a temperature of 30°C. to a total dose of 8 megarads, then the tubing was placed under stress in the machine and the transverse directions at 100° to 120°C. and cooled while maintaining the stress. The percent shrink and the shrink tension of the biaxially oriented, irradiated film are shown in Table IV.

TABLE IV

Temperature of Shrinking °C.	Percent Shrink			Shrink Tension kg/sq. cm.	
	Length	Width	Area	Length	Width
96	45	55	75	—	—
98	47	61	79	4.2	3.09
101	65	72	90	—	—

— (not measured)

EXAMPLE 9

An ethylene copolymer containing 12 percent of vinyl acetate and having a density of 0.925 was irradiated and biaxially oriented by the procedure of Example 1 then the film was

shrunk at 98°C. in the longitudinal (machine) and in the transverse directions. The creep or elongation under static stress was determined at various intervals of time. The results are shown in Table V.

TABLE V

Percent Elongation Under Static Stress

Time Under Stress (Hrs.)	Stress, 17.5 kg/sq. cm.		Stress, 34.5 kg/sq. cm.	
	Transverse (45 Percent Shrink)	Longitudinal (36 Percent Shrink)	Transverse (45 Percent Shrink)	Longitudinal (36 Percent Shrink)
0.2	2.4	3.2	11.3	7.5
1	2.6	3.6	13.0	9.0
4	3.2	4.0	14.8	11.8
20	3.6	4.3	16.0	13.1

EXAMPLE 10

Irradiated, biaxially oriented ethylene copolymer films containing different amounts of the minor component were tested for impact

resistance by the method of ASTM D-1709 5
59T modified to allow the use of dart weights in excess of 1000 grams. The results are shown in Table VI.

TABLE VI

Ethylene Copolymer Film		Melt Index	Dose (Megarads)	Impact ft. lb./mil. (kg./meters/0.025 mm.)
Minor Component	Percent			
None (Homopolymer)*	0	2.0	5	0.4 (0.055)
Ethyl acrylate	10	2.0	5	2.2 (0.34)
Ethyl acrylate	20	2.0	5	5.2 (0.72)
Acrylic acid	5	2.0	5	2.2 (0.34)
Acrylic acid	10	2.0	5	1.8 (0.25)

* Not an example of this invention.

10

EXAMPLE 11

An ethylene copolymer containing 6 percent of interpolymerized vinyl acetate and having a melt index of 2.0 was extruded at a temperature of 160°C., through a slit die, to form a flat film having a thickness of 15 mils (0.38 mm.). The flat film was irradiated by the procedure of Example 1 so that different sections of the film received doses of 4 megarads, 8 megarads, and 12 megarads, respectively.

Samples, 4" x 4" (10 x 10 cm.), were stretched 20
in a plane at 100°C. to a size of 12" x 12" x 1.7 mils (30.48 x 30.48 cms. x 0.43 mm.) in a machine designed to hold and to stretch film in a heated chamber (the T. M. Long Film 25
Stretcher). After the samples were cooled under tension the percent shrink (longitudinal direction) and the shrink tension were measured with the results shown in Table VII.

TABLE VII

Irradiation Dose (Megarads)	Percent Shrink in Length at			Shrink Tension (Gm/in ²) Gm/6.45 sq. cm. at	
	98° C.	101° C.	104° C.	96° C.	101° C.
4	32	52	65	58,000	52,000
8	36	55	67	44,000	49,000
12	45	61	67	43,000	48,000

30 The products provided by the invention also have the commercially desirable advantage of an unusually "soft feel".

WHAT WE CLAIM IS:—

1. Process for making a shrinkable film from a polymer comprising the steps of:
 - (a) making a thin, coherent film of a polymer comprising in interpolymerized form a major amount of ethylene and a minor amount of at least one monovinylidene monomer which is a vinyl ester of a C_1 to C_4 alkanolic monobasic acid, a C_1 to C_4 alkyl ester of an α,β -ethylenically unsaturated monocarboxylic acid, an α,β -ethylenically unsaturated monocarboxylic acid or an α,β -ethylenically unsaturated nitrile,
 - (b) irradiating the extruded polymer film with a dose of ionizing radiation of from 1 to 20 megarads,
 - (c) placing the irradiated film under stress to produce orientation by stretching in at least one direction while the film is maintained at a temperature of from 85° to 200°C. and
 - (d) cooling the film to below 70°C. while maintaining said stress.
2. Process of Claim 1 in which the dose of ionizing radiation is from 2 to 10 megarads.
3. Process of Claim 1 in which the interpolymerized monovinylidene monomer is from 1 to 45 percent by weight of the copolymer.
4. Process of Claim 3 in which the interpolymerized monovinylidene monomer is from 3 to 20 percent of the copolymer.
5. Process of any one of Claims 1 to 3 in which the monovinylidene monomer is vinyl acetate, ethyl acrylate, acrylic acid, or acrylonitrile.
6. Process for making copolymer shrinkable films substantially as hereinbefore described with reference to the specific examples.
7. Shrinkable film whenever made by the process of any one of Claims 1 to 6.

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